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MOD SILVER METALLIZATION FOR PHOTOVOLTAICS

Purdue Research Foundation

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JPL Flat Plate Solar Array Project

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## 1. INTRODUCTION AND OBJECTIVES

Photovoltaic cells require back side metallization and a collector grid system on the front surface. Both front and back surface metallizations should have good adhesion, low contact resistance, low sheet resistance, long term stability, and their deposition methods should not degrade the n-p junction. In addition, the metallization for the collector grid should be capable of producing small grid spacings and grid widths. For the terrestrial flat-plate solar array project, low cost of the metallization is also a very important requirement. One of the dominant systems in use today is screen printed thick film silver conductors. When such conductors are used in hybrid microelectronics they are typically fired at temperatures from 650-800<sup>o</sup>C for 10-15 minutes, but for solar cells they must be rapidly fired in order to avoid degradation of the junction. This rapid firing compared to the conditions for which the inks were developed often leads to poor adhesion, and porous silver films are always the result. In addition, typical frit bonded thick film silver conductors present a problem because the frit dissolves the SiO<sub>2</sub> film on the photovoltaics and sometimes produces a reaction layer down to the junction.

Metallo-organic compounds are ones in which a metal atom is linked to a long chain carbon ligand through a hetero atom such as O, S, N, P or As. In order that the products of decomposition contain only CO<sub>2</sub>, H<sub>2</sub>O and perhaps nitrogen compounds, Purdue's Turner Laboratory pioneered the use of a set of metallo-organic compounds for ink fabrication where the linking hetero atom was oxygen. Inks were made from commercially

available carboxylates or synthesized from commonly available reagents. Films produced by the metallo-organic decomposition (MOD) process have a number of advantages compared to conventional thick films. Advantages concerning performance in service are discussed in the following paragraph, but an additional advantage of the approach followed at Purdue is that the research will lead to generic inks. Even if conventional inks did not contain proprietary additives they still could not be duplicated in the user's laboratory because film properties are dependent on characteristics of the particulates (average particle size, particle size distribution, particle shape, etc.) in addition to their chemical composition.

All chemical compounds are in solution in inks for the MOD process, which means the mixing of the inorganic constituents is achieved on an atomic scale, and films produced after decomposition of the organic compounds reflect this uniformity. The uniformity of conventional thick films is a strong function of the degree of blending of the particulates in the organic screening agents. Even if ideal blending could be achieved (which is impossible with particulates of differing density in a gravitational field) there is always an inherent nonuniformity due to the finite particle sizes of the different constituents in the inks. For a fritted conductor, conventional thick film inks will always lead to films having voids in the metal network where glass particles had initially been after film deposition.

Films produced by the MOD process are inherently thinner than films produced by conventional thick film technology because the volume change from wet to fired MOD film is typically a factor of 50 compared to a

factor of 3 for conventional thick films. This can be a disadvantage if very high conductance is required, but can partially be overcome by deposition of thicker films. Because the extremely high viscosity required to keep particulates in suspension is not a requirement for MOD inks, a wide range of viscosities is possible and any one of the various printing technologies is feasible for deposition.

MOD silver films have the potential for eliminating most of the present problems with silver conductors. Preliminary results indicate that the MOD silver films can be produced at much lower firing temperatures (e.g. 250<sup>o</sup>C) and achieve very good adhesion without a glassy phase present. This should eliminate chemical interaction effects as well as detrimental thermal effects on the junction. In addition, research on other MOD conductor films has demonstrated that this approach can produce theoretically dense metal films which would eliminate the porosity associated problems.

The specific technological objectives of the current program are to develop screen printable MOD silver inks and suitable processing conditions to produce grid patterns on photovoltaic cells. The metallizations will be evaluated as to their line definition, adhesion, sheet resistance and microstructure. The adhesion and sheet resistance will also be evaluated after thermal aging. Another objective of the program is to develop a model which describes the adhesion between the MOD silver film and the silicon surface.

## 2. SUMMARY

It was determined that pyrolysis products can produce dark surface films on MOD silver conductors. Improving the purity of all ink ingredients helped this problem. It was established that the existence and nature of the surface film is influenced by the rate of air flow during firing and by the heating rate in the 70-225<sup>o</sup>C range, but these processing parameters have not as yet been optimized.

Low temperature solvent removal was determined to be of prime importance in obtaining good adhesion between the MOD films and the substrate. For inks developed to date, 15-30 minutes at 60-70<sup>o</sup>C was required. It was also determined that the adhesion is influenced by the air flow rate during firing, the heating rate in the 100-250<sup>o</sup>C range, and the maximum firing temperature.

Results during the first 3 months of effort on this project have demonstrated that it is essential to use generic compounds, and that the compounds must be prepared from high purity raw materials. It was also established that the quality and properties of the MOD silver films are intimately dependent on the time-temperature processing. All of the results obtained to date still indicate that MOD silver shows great promise for low temperature metallization of photovoltaic cells.



### 3. EXPERIMENTAL

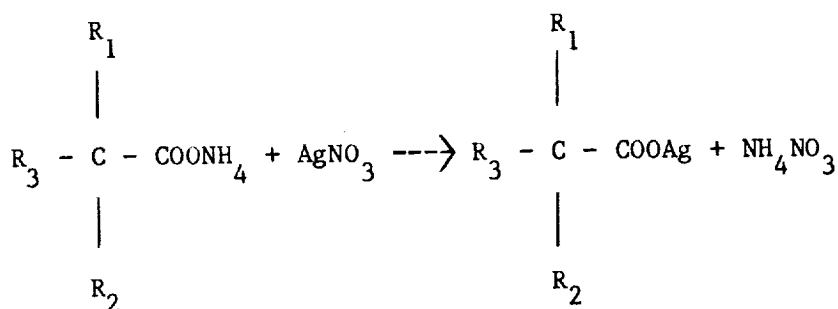
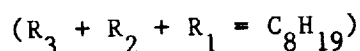
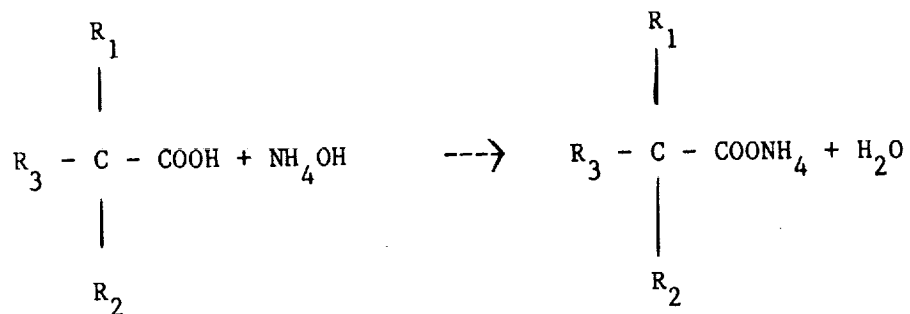
#### 3.1 Synthesis of Compounds

The initial objective was to synthesize various silver carboxylates in order to select a suitable one which would satisfy most of the requirements for a good silver MOD film. Silver carboxylates were chosen due to the fact that they decompose at low temperatures with the by-products consisting of only carbon, hydrogen and oxygen (as  $\text{CO}_2$ , hydrocarbons, etc.). The requirements for the compounds were:

1. they should be in a suitable molecular weight range in order to produce 30-50 w/o of silver on decomposition;
2. they should be fairly soluble in low boiling point hydrocarbon solvents (either aromatic or aliphatic or both);
3. they should be completely miscible with the vehicle or additive used, and should not chemically react with the additive:  
and
4. all chemicals and solvents used should be as pure as possible.

The following silver carboxylates were prepared: a) silver monomethyl succinate; b) silver 2-ethylbutyrate; c) silver 2-ethylhexanoate; d) silver neopentanoate; and e) silver neodecanoate. These compounds were selected because they contained primary (a), secondary (b and c) and tertiary (d and e) ligands with chain length varying from  $\text{C}_5$  to  $\text{C}_{10}$ . All of the silver compounds were synthesized following the same procedure. Synthesis of silver neodecanoate is described as

representative. The reactions were:

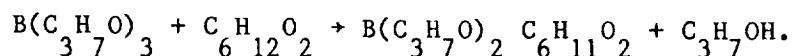


An equimolar mixture of 95% pure neodecanoic acid (9.46 gm = 0.055 mole) and 58% ammonium hydroxide (3.31 gm = 0.055 mole) were mixed together at room temperature and the resulting soap was diluted in deionized water (50 ml). An aqueous solution of silver nitrate (10 g = 0.0526 mole) (water = 50 ml) was then added slowly with stirring. The white precipitate of silver neodecanoate thus formed was repeatedly washed with cold and warm (30-50°C) deionized water. The solid was mixed with methanol (100 ml) for a final drying and purification, stirred well and suction filtered. The average yield was 70%.

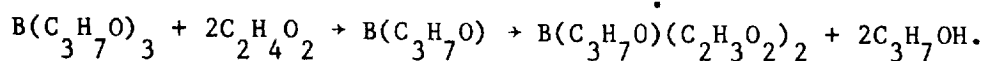
Two boron compounds and a silicon compound were synthesized for evaluation as adhesion promoters. The apparatus consisted of a 500 ml

3-neck reaction vessel equipped with a heating mantle, and a magnetic stirrer unit. One neck was used for inserting a thermometer, and another for entering chemicals via a funnel or for mounting a separatory funnel as a sealed liquid dispenser during operation. The third neck connected to a reflux condensor (mounted at a 45° angle) with a claisen head, and led by means of a water-cooled spiral condensor to a 1000 ml 3-neck waste collection vessel. One of the necks of the waste vessel connected via a suction hose to a cold trap, a control valve, and a vacuum pump capable of achieving a vacuum for less than 0.05 torr. The third neck of the waste vessel led to a pressure gauge, and via a cutout valve vented the system through a drierite column to the ambient.

The first boron compound synthesized was boron-bis-n-propoxy-2-ethylbutyrate (BBPE) according to the reaction:

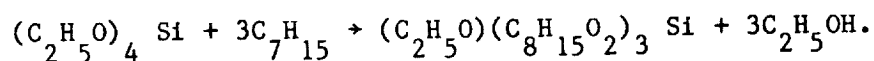


A 1:1 mole ratio of tri-n-propyl borate (50 ml) and 2-ethyl butyric acid (30 ml) were mixed together in the reaction vessel and heated to 130°C while stirring. The system was flushed with N<sub>2</sub> gas to remove the alcohol by-product. Toward the end of the reaction the pressure was reduced to 0.05 torr after sealing the N<sub>2</sub> inlet for additional alcohol removal from the reaction vessel. The system was finally vented through a drierite column. The second boron compound synthesized was boron-n-propoxy diacetate (BPDA) according to the following reaction:



This compound was prepared in the same manner as BBPE except that acetic acid was used instead of 2-ethylbutyric acid.

The silicon compound was ethoxy-silicon-tri 2-ethylhexanoate (ESIE) synthesized by the reaction:



After removing the moisture from the synthesis apparatus, the 2-ethylhexanoic acid was placed in the reaction flask that contained boiling chips. The tetraethoxy silane was sealed in a 250 ml separatory funnel with a 2 mm stopcock bore and mounted over the reaction vessel. The acid was heated to the boiling point ( $225^\circ\text{C}$  at 1 atm) and the tetraethoxy silane was dripped into the boiling acid at a rate of approximately 4 ml/min. After all of the tetraethoxy silane was added, the flask was cooled to  $110^\circ\text{C}$  and held there while the pressure was reduced to 1 torr and the volatile components were boiled off. The system was vented through the drierite column then cooled to room temperature before exposing the pale yellow liquid to the moisture in the air. Toluene (4 ml) was added to prevent gel formation.

The source and cost of all reagents used in synthesis of the various compounds are given in Table 3.1.

### 3.2 Characterization of Ink Ingredients

The five silver metallo-organic compounds synthesized as described in Section 3.1 were subjected to thermogravimetric analysis (TGA) at a heating rate of  $10^\circ\text{C}/\text{minute}$ . The results are shown in Figs. 3.1-3.5

Table 3.1 Reagents Used in Synthesis of Metallo-Organic Compounds

Chemical	Formula	Source	Cost
Silver nitrate	$\text{AgNO}_3$	J.T. Baker	42.70/4 oz.
Ammonium hydroxide	$\text{NH}_4\text{OH}$	Mallinckrodt	5.57/4 lb.
Mono-Methyl Succinate	$\begin{array}{c} \text{CH}_2-\text{COOCH}_3 \\   \\ \text{CH}_2 \text{ COOH} \end{array}$	Aldrich	24.10/100 g.
2-Ethyl butyric acid	$\begin{array}{c} \text{C}_2\text{H}_5-\text{CH}-\text{COOH} \\   \\ \text{C}_2\text{H}_5 \end{array}$	Aldrich	7.75/100 g.
Neopentanoic acid	$\begin{array}{c} \text{CH}_3 \\   \\ \text{H}_3\text{C}-\text{C}-\text{COOH} \\   \\ \text{CH}_3 \end{array}$	Exxon	gift
2-Ethyl hexanoic acid	$\begin{array}{c} \text{C}_2\text{H}_5 \\   \\ \text{C}_4\text{H}_9-\text{C}-\text{COOH} \\   \\ \text{H} \end{array}$	Exxon	gift
Neodecanoic acid	$\text{C}_9\text{H}_{19}\text{COOH}$	Exxon	gift
Methanol	$\text{CH}_3\text{OH}$	Fisher	2.48/Qt
Tri-n-propyl borate	$(\text{C}_3\text{H}_7\text{O})_3\text{B}$	Alfa	25.10/250 g.
Tetraethoxy silane	$(\text{C}_2\text{H}_5\text{O})_4\text{Si}$	Alfa	15.80/500 g
Toluene	$\text{C}_7\text{H}_8$	Mallinckrodt	1.58/1 pt.
Xylene	$\text{C}_8\text{H}_{10}$	Mallinckrodt	22.23/5 gal.
Acetic acid (glacial)	$\text{CH}_3\text{COOH}$	Mallinckrodt	8.57/5 lb.

P.N. 25693

RUN NO. Jan 3rd '84 DATE  
 OPERATOR Sara Siganam  
 S' Silver monomethyl succinate  
 ATM air 1.1 1.2 (solid)  
 FLOW RATE 20 cm/min

T-AXIS  
 PROG. RATE, °C/min 10  
 RANGE, °C/cm. 25  
 HEAT COOL ISO  
 SHIFT, cm. ±10  
 TIME, min/cm 5

DSC 200 μW/mV  
 DTA 50 mK/mV  
 RANGE, mV/cm  
 WEIGHT, mg  
 REFERENCE

TGA 50 μg/mV DTG 50 μg/(min mV)  
 SUPPRESSION, mg  
 RANGE, mV/cm  
 WEIGHT, mg  
 TIME CONST., sec  
 dY

TMA 1 μm/mV DTM 0.1 μm/(min mV)  
 MODE  
 RANGE, mV/cm  
 SAMPLE SIZE  
 LOAD, g  
 dY

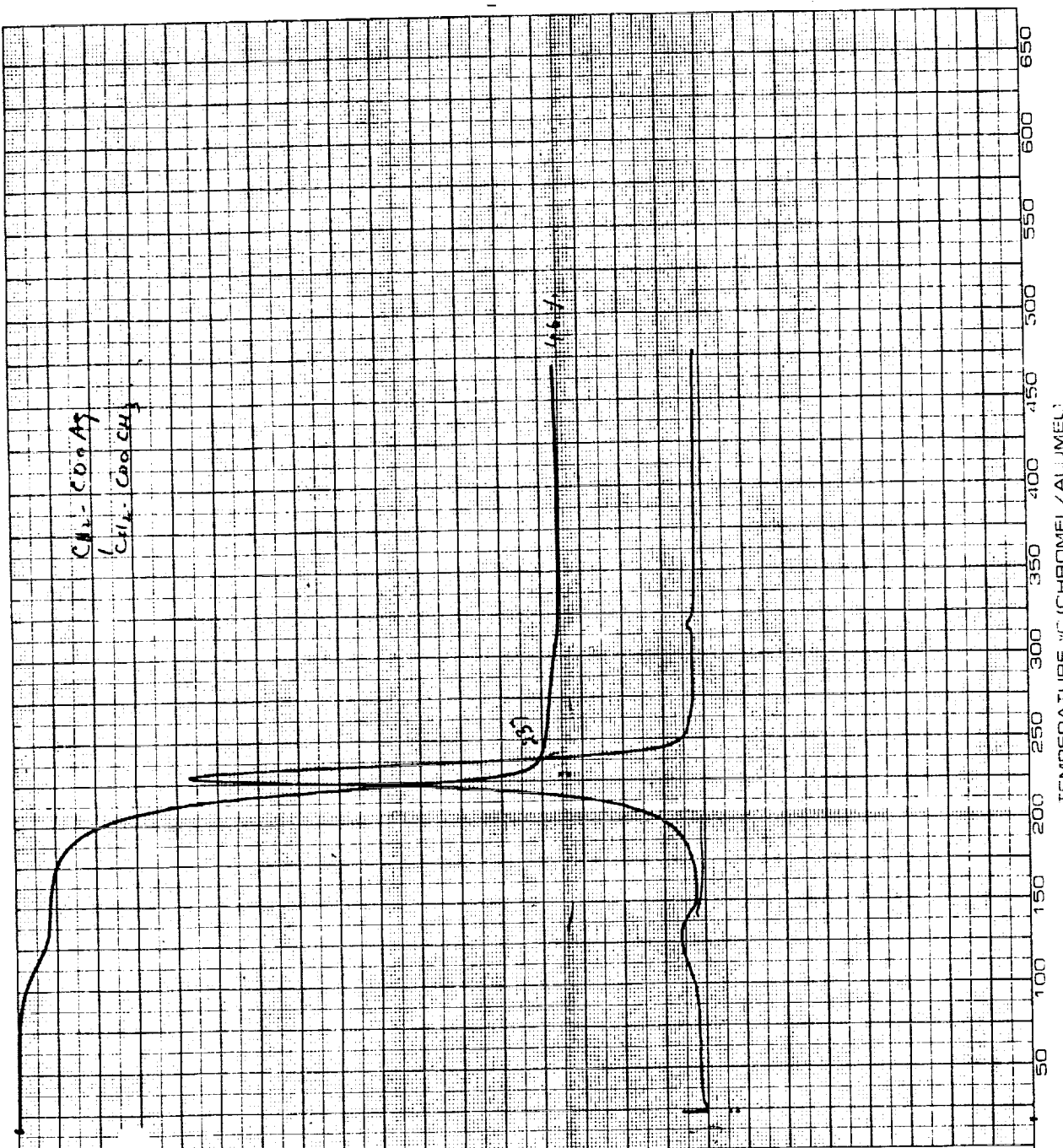


Figure 3.1 Thermogram of Silver Monomethyl Succinate.



P.N. 25693

RUN NO. \_\_\_\_\_ DATE Jan 3 '84  
 OPERATOR S. A. Lippman  
 SAMP Silver 2-ethylbutyrate  
 ATM air  
 FLOW RATE 70 cm/min (Solid)

## T-AXIS

PROG. RATE, °C/min 10  
 RANGE, °C/cm 25  
 HEAT COOL ISO  
 SHIFT, cm +10  
 TIME, min/cm 5

DSC 200  $\mu$ W/mV

DTA 50 mK/mV

RANGE, mV/cm \_\_\_\_\_

WEIGHT, mg \_\_\_\_\_

REFERENCE \_\_\_\_\_

TGA 50  $\mu$ g/mV DTG 50  $\mu$ g/(min mV)

SUPPRESSION, mg \_\_\_\_\_

RANGE, mV/cm \_\_\_\_\_

WEIGHT, mg \_\_\_\_\_

TIME CONST., sec \_\_\_\_\_

dY \_\_\_\_\_

TMA 1  $\mu$ m/mV DTM 0.1  $\mu$ m/(min mV)

MODE \_\_\_\_\_

RANGE, mV/cm \_\_\_\_\_

SAMPLE SIZE \_\_\_\_\_

LOAD, g \_\_\_\_\_

dY \_\_\_\_\_

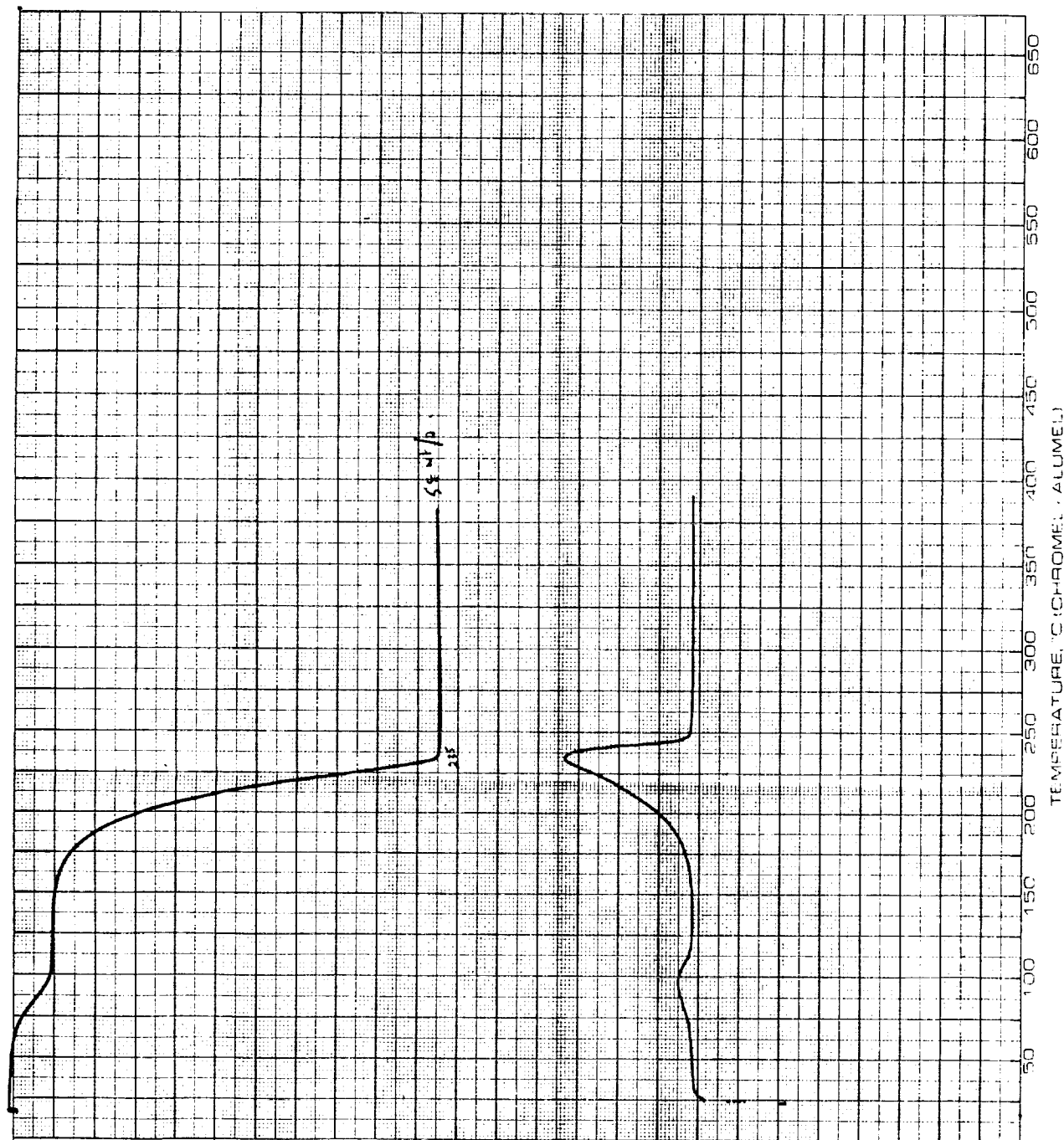


Figure 3.2 Thermogram of Silver 2-ethylbutyrate.

P.N. 25693

RUN NO. Jan 3rd 64 DATE Jan 3rd 64  
 OPERATOR Jan 3rd 64  
 SAMPLE Silver 2-ethylhexanoate  
 ATM Cell @ (Solid)  
 FLOWRATE 70 cm/min

## T-AXIS

PROG. RATE, °C/min 10  
 RANGE, °C/cm 25  
 HEAT COOL ISO  
 SHIFT, cm +10  
 TIME, min/cm 5

DSC 200  $\mu$ W/mV

DTA 50 mK/mV

RANGE, mV/cm

WEIGHT, mg

REFERENCE

TGA 50  $\mu$ g/mV DTG 50  $\mu$ g/(min mV)

SUPPRESSION, mg

RANGE, mV/cm

WEIGHT, mg

TIME CONST., sec

dY

TMA 1  $\mu$ m/mV DTM 0.1  $\mu$ m/(min mV)

MODE

RANGE, mV/cm

SAMPLE SIZE

LOAD, g

dY

TEMPERATURE, °C (CHROMEL/ALUMEL)

Figure 3.3 Thermogram of Silver 2-ethylhexanoate.





P.N. 25693

RUN NO.	DATE	Jan 3 '84
OPERATOR	Lara S. Saram	
SAMPLE	Silver neopentanoate	
ATM.	Air	(solid)
FLOW RATE	70	

T-AXIS	
PROG. RATE, °C/min	20
RANGE, °C/cm	25
HEAT	COOL ISO
SHIFT, cm	+10
TIME, min/cm	

DSC	200 $\mu$ W/mV
DTA	50 mK/mV
RANGE, mV/cm	
WEIGHT, mg	
REFERENCE	

TGA	50 $\mu$ g/mV	DTG	50 $\mu$ g/(min mV)
SUPPRESSION, mg			
RANGE, mV/cm			
WEIGHT, mg			
TIME CONST., sec			
dY			

TMA	1 $\mu$ m/mV	DTM	0.1 $\mu$ m/(min mV)
MODE			
RANGE, mV/cm			
SAMPLE SIZE			
LOAD, g			
dY			

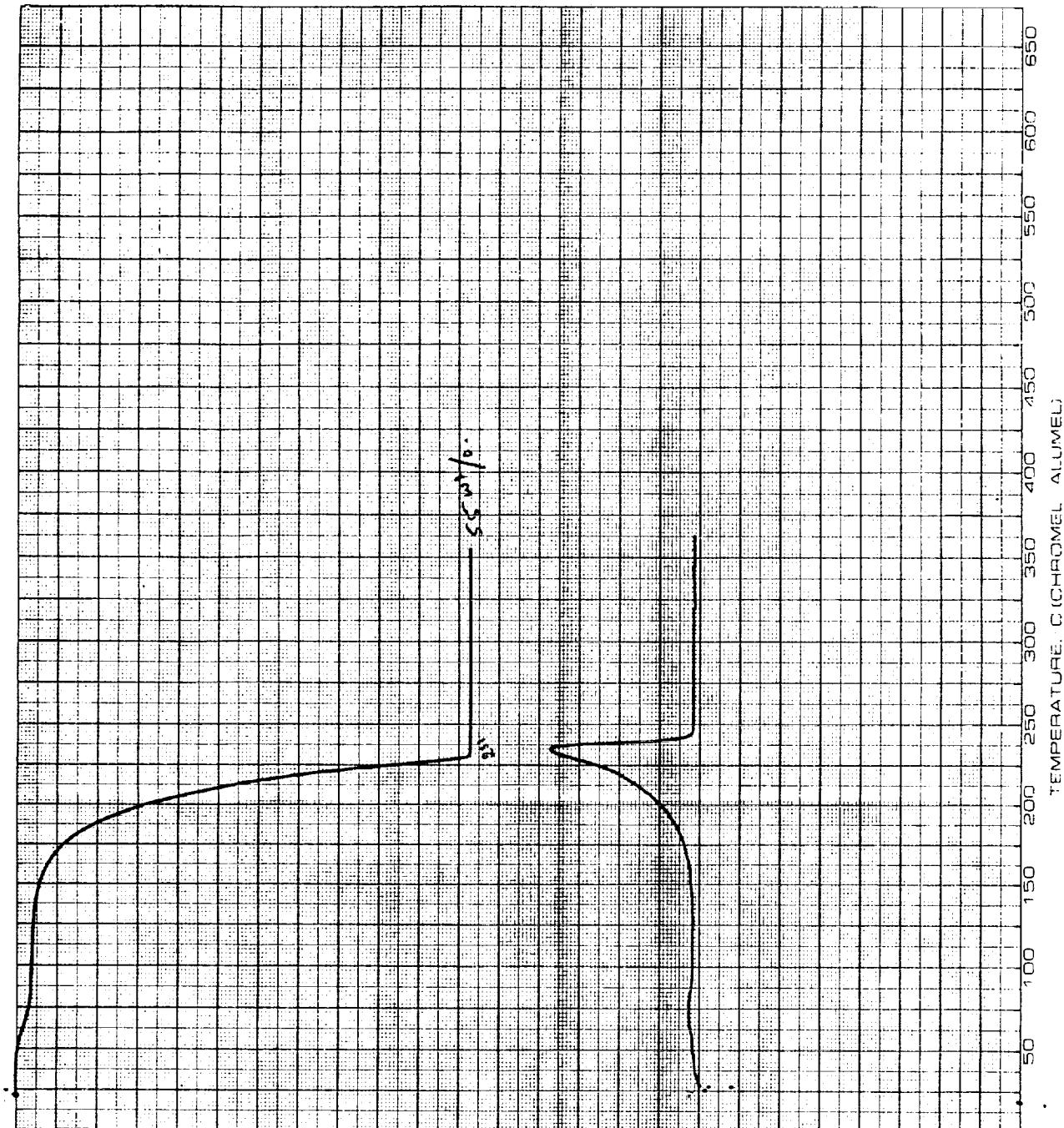


Figure 3.4 Thermogram of Silver Neopentanoate.



P.N. 25693

RUN NO. DATE 1/12/54OPERATOR SoloSAMPLE Silver neodecanoate (solid)ATM 21FLOW RATE 16

## T-AXIS

PROG. RATE, °C/min 10RANGE, °C/cm 25HEAT COOL ISOSHIFT, cm \*10 5TIME, min/cm 5DSC 200  $\mu$ W/mVDTA 50 mK/mV

RANGE, mV/cm

WEIGHT, mg

REFERENCE

TGA 50  $\mu$ g/mV DTG 50  $\mu$ g/(min mV)

SUPPRESSION, mg

RANGE, mV/cm

WEIGHT, mg

TIME CONST., sec

dY

TMA 1  $\mu$ m/mV DTM 0.1  $\mu$ m/(min mV)

MODE

RANGE, mV/cm

SAMPLE SIZE

LOAD, g

dY

TEMPERATURE, °C (CHROMEL/ALUMEL)

Figure 3.5 Thermogram of Silver Neodecanoate (solid).

where the upper curve is the relative weight from 0 to 100%, and the lower curve is the derivative of the weight with respect to temperature. The decomposition temperatures were taken as the temperature corresponding to the maximum rate of weight loss (the peak in the derivative curve). The amount of silver produced and the decomposition temperatures of the 5 silver compounds are summarized in Table 3.2. The amount of silver produced was in general agreement with the theoretical values calculated from the chemical formulae. All of the compounds had approximately the same decomposition temperature (230-235°C) even though the molecular weight and the degree of branching varied considerably. This suggests that the decomposition is initiated in all of the compounds by breaking of the silver-oxygen bond. If this is true, then all silver carboxylates will decompose at 230-235°C, which means that other ink constituents (e.g. solvents or additives to control rheology) must be removed below this temperature to avoid disruption of the Ag film.

Of the 5 compounds listed in Table 3.2 only silver neodecanoate showed appreciable solubility in hydrocarbon solvents. This observation is in general agreement with the rule-of-thumb that solubility increases with chain length and degree of branching. Silver monomethyl succinate and silver 2-ethyl hexanoate showed an additional small weight change between 230 and 300°C (see Figs. 3.1 and 3.3), which indicates that the decomposition is not as clean as with the other compounds. Based on all of these results, silver neodecanoate was selected as the most suitable compound.

The solvents considered for screen printing inks are listed in Table 3.3 along with their boiling points, suppliers and costs. The

Table 3.2 TGA Results for Five Silver Compounds.

Silver Compound	Formula	w/o Ag		$T_d(^{\circ}\text{C})$
		(theo)	(expl)	
Mono-methyl succinate	$\text{CH}_3\text{OOC} \cdot \text{C}_2\text{H}_4 \cdot \text{COOAg}$	45	46	230
2-Ethyl butyrate	$\text{C}_2\text{H}_5 - \overset{\overset{\text{C}_2\text{H}_5}{ }}{\underset{\underset{\text{H}}{ }}{\text{C}}} - \text{COOAg}$	48	58	235
2-Ethyl hexanoate	$\text{C}_4\text{H}_9 - \overset{\overset{\text{H}}{ }}{\underset{\underset{\text{C}_2\text{H}_5}{ }}{\text{C}}} - \text{COOAg}$	43	42	235
Neopentanoate	$\text{CH}_3 - \overset{\overset{\text{CH}_3}{ }}{\underset{\underset{\text{CH}_3}{ }}{\text{C}}} - \text{COOAg}$	52	55	230
Neodecanoate	$\text{R}_3 - \overset{\overset{\text{R}_1}{ }}{\underset{\underset{\text{R}_2}{ }}{\text{C}}} - \text{COOAg}$	38.6	38	230
$[\text{R}_1 + \text{R}_2 + \text{R}_3 = \text{C}_8\text{H}_{19}]$				

Table 3.3 Solvents Considered for Screen Printing Inks.

Commercial Name	Chemical Name	Formula	Boiling Point	Source	Cost
Butyl carbitol acetate	2-(2-butoxyethoxy) ethyl acetate	$\text{CH}_3(\text{CH}_2)_3 \cdot \text{O} \cdot \text{CH}_2\text{CH}_2 \cdot \text{O} - \text{CH}_2 - \text{CH}_2 \text{COOCH}_3$	236-249°	Fisher Scientific Co.	16.75/500 ml
Butyl carbitol acetate	$\alpha$ -Terpineol	$\text{CH}_3(\text{C}_6\text{H}_8)\text{C}(\text{CH}_3)_2\text{OH}$	217-218°	Fisher Scientific Co.	32.05/1 lit
Phenyl ether	Diphenyl ether	$(\text{C}_6\text{H}_5)_2\text{O}$	259°	Aldrich	14.15/1 kg
Dodecane	Dodecane	$\text{CH}_3(\text{CH}_2)_{10}\text{CH}_3$	215-17°	Aldrich	9.15/100 g
Diglyme	2-Methoxy ethyl ether	$(\text{CH}_3\text{OCH}_2\text{CH}_2)_2\text{O}$	162°	Aldrich	16.50/500 g
Triglyme	Tri ethylene glycol dimethyl ether	$\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{O} - \text{CH}_2\text{CH}_2\text{OCH}_3$	216°	Aldrich	12.70/250 g
Neodecanoic acid	Neodecanoic acid	$\begin{array}{c} \text{R}_1 \\   \\ \text{R}_2 - \text{C} - \text{COOH} \\   \\ \text{R}_3 \end{array}$	250-257°	Exxon	gift
$[\text{R}_1 + \text{R}_2 + \text{R}_3 = \text{C}_8\text{H}_{19}]$					

fact that some of the solvents have boiling points above the decomposition temperature of silver neodecanoate does not necessarily mean that they are not suitable. For example, the thermograms of butyl carbitol acetate and neodecanoate acid, shown in Figs. 3.6 and 3.7 respectively, demonstrate that both solvents are completely vaporized approximately  $100^{\circ}\text{C}$  below their boiling points when heated at  $10^{\circ}\text{C}/\text{minute}$ .

### 3.3 Ink Formulation and Deposition

The following general methods were used in making the silver inks.

#### METHOD A:

A xylene solution of silver neodecanoate with known w/o of silver was mixed with the additive, either neat or in xylene solution, to give at least 25 w/o of Ag in the final ink. The solvents were stripped off at  $40\text{--}60^{\circ}$  using rotary vacuum evaporation. The viscous residue left had almost the right rheology for screen printing if the proper amount of additive was used.

#### METHOD B:

A toluene solution of silver neodecanoate was used instead of a xylene solution, but otherwise the procedure of Method A was followed.

#### METHOD C:

Solid silver neodecanoate was mixed with the additive to get the correct ink rheology.

P.N. 25693

RUN NO. \_\_\_\_\_ DATE 2/15/81  
 OPERATOR Sabo  
 SAMPLE Butyl Carbitol Acetate  
 ATM air @ \_\_\_\_\_  
 FLOW RATE 70

T-AXIS

PROG. RATE, °C/min 10  
 RANGE, °C/cm 25  
 HEAT \_\_\_\_\_ COOL \_\_\_\_\_ ISO \_\_\_\_\_  
 SHIFT, cm +10  
 TIME, min/cm 5

DSC 200  $\mu$ W/mV

DTA 50 mK/mV

RANGE, mV/cm \_\_\_\_\_

WEIGHT, mg \_\_\_\_\_

REFERENCE \_\_\_\_\_

TGA 50  $\mu$ g/mV DTG 50  $\mu$ g/(min mV)

SUPPRESSION, mg \_\_\_\_\_

RANGE, mV/cm \_\_\_\_\_

WEIGHT, mg \_\_\_\_\_

TIME CONST., sec \_\_\_\_\_

dY \_\_\_\_\_

TMA 1  $\mu$ m/mV DTM 0.1  $\mu$ m/(min mV)

MODE \_\_\_\_\_

RANGE, mV/cm \_\_\_\_\_

SAMPLE SIZE \_\_\_\_\_

LOAD, g \_\_\_\_\_

dY \_\_\_\_\_

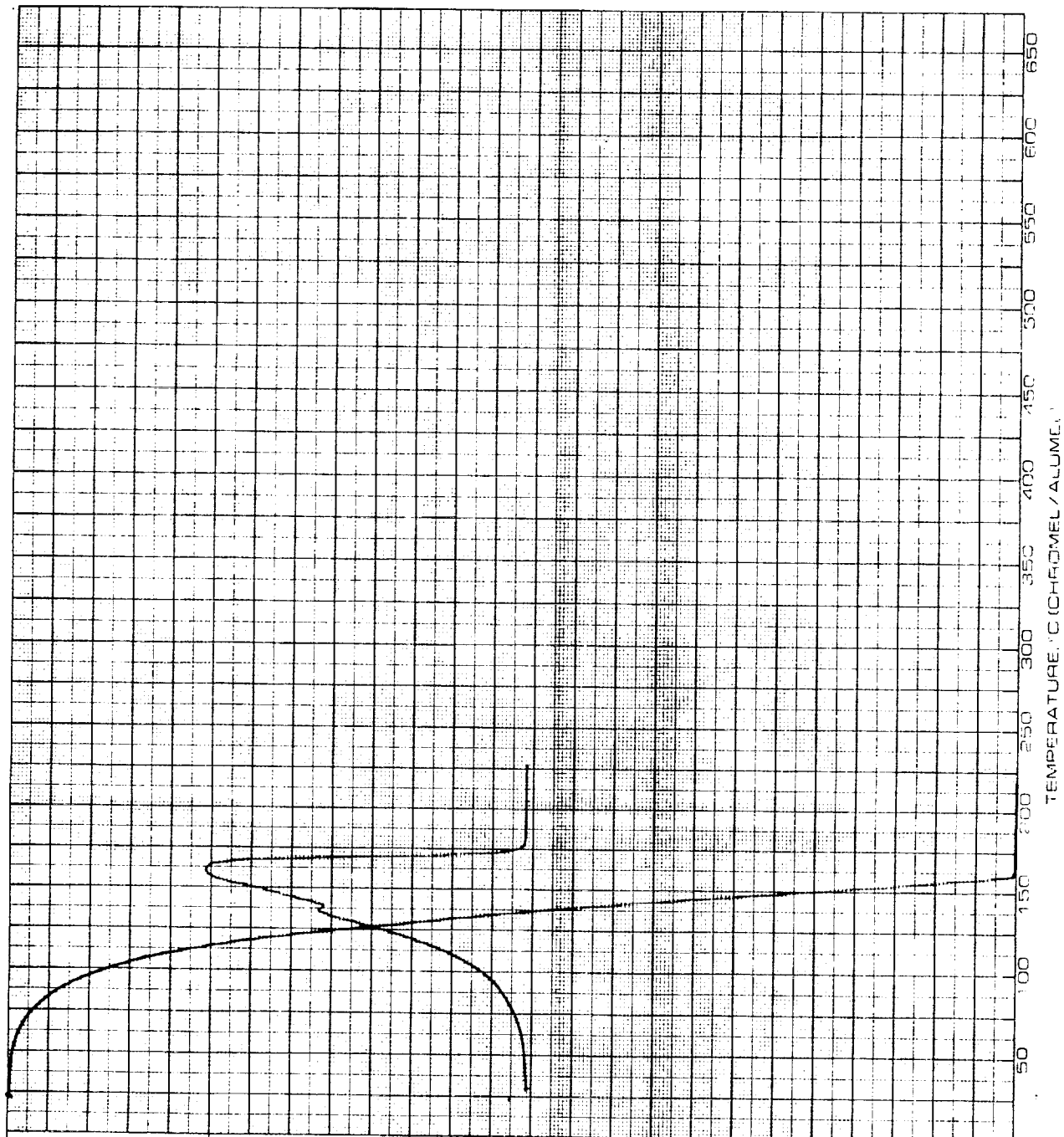


Figure 3.6 Thermogram of Butyl Carbitol Acetate.



P.N. 25693

RUN NO. DATE 2/17/83

OPERATOR Sabo

SAMPLE Neodecanoic Acid

ATM Air @

FLOW RATE 70 °C/min

## T-AXIS

PROG. RATE, °C/min 10

RANGE, °C/cm 25

HEAT COOL ISO

SHIFT, cm. ±10

TIME, min/cm 5

DSC 200 µW/mV

DTA 50 mK/mV

RANGE, mV/cm

WEIGHT, mg

REFERENCE

TGA 50 µg/mV DTG 50 µg/(min mV)

SUPPRESSION, mg

RANGE, mV/cm

WEIGHT, mg

TIME CONST., sec

dY

TMA 1 µm/mV DTM 0.1 µm/(min mV)

MODE

RANGE, mV/cm

SAMPLE SIZE

LOAD, g

dY

TEMPERATURE, °C (CHROMEL/ALUMEL)

Figure 3.7 Thermogram of Neodecanoic Acid.





The first additive evaluated was nitrocellulose because it is similar to the high molecular weight screening agents used in conventional thick film inks but it decomposes at a lower temperature. Figure 3.8 is a thermogram of that ink, and shows that the major weight change occurs below 250°C as expected. However, there is a "tail" to the curve in the 240 to 360°C range which indicates that additional material is being vaporized. This is an undesirable situation because the silver film formed by 250°C will be disrupted.

The next approach evaluated was to develop inks with only solvent additives, and to rely on the silver neodecanoate to impart the required high viscosity. The method of preparation, compositions and some properties of the inks prepared are given in Table 3.3. The temperature for complete carbon removal was determined from the TGA of each ink. In a few cases the TGA of the ink was nearly a superposition of the TGA's of the constituents. For example, Fig. 3.9 is a thermogram of Ink No. 9, which contains only silver neodecanoate and neodecanoic acid, and shows the mixture of the two constituents behaving in a manner similar to the pure compounds (Fig. 3.5 and 3.7). The decomposition temperature of Ag neodecanoate is 230°C in both the pure state (Fig. 3.5) and in Ink No. 9 (Fig. 3.9), and the temperature of maximum vaporization of neodecanoic acid is increased only from 137°C in the pure state (Fig. 3.7) to 170°C in the ink (Fig. 3.9). Some other inks showed behavior significantly different from that of the constituents alone. For example, Ink No. 3 contained only silver neodecanoate and phenyl ether solvent. Individually, the phenyl ether was completely vaporized by 175°C and the silver neodecanoate completely decomposed by 230°C when heated at

P.N. 25693

Jan 12 '84

DATE

OPERATOR: Sara S. Tanam

SAMPLE: Silver neodecanoate +  
nitro cellulose

ATM

FLOW RATE: 50

T-AXIS

PROG RATE, °C/min 10

RANGE, °C/cm 25

HEAT COOL ISO

SHIFT, cm +10

TIME, min/cm 5

OSC 200  $\mu$ W/mV

DTA 50 mK/mV

RANGE, mV/cm

WEIGHT, mg

REFERENCE

TGA 50  $\mu$ g/mV DTG 50  $\mu$ g/(min mV)

SUPPRESSION, mg

RANGE, mV/cm

WEIGHT, mg

TIME CONST., sec

dY

TMA 1  $\mu$ m/mV DTM 0.1  $\mu$ m/(min mV)

MODE

RANGE, mV/cm

SAMPLE SIZE

LOAD, g

dY

TEMPERATURE, °C (DOWN) ALUMINUM

Figure 3.8 Thermogram of Silver Ink with Nitrocellulose Screening Agent.



P.N. 25693

RUN NO. DATE 1/31/64  
 OPERATOR Sura  
 SAMPLE Ag # 9 (neodecanoic acid)  
 ATM Air  
 FLOW RATE 70 cm/min

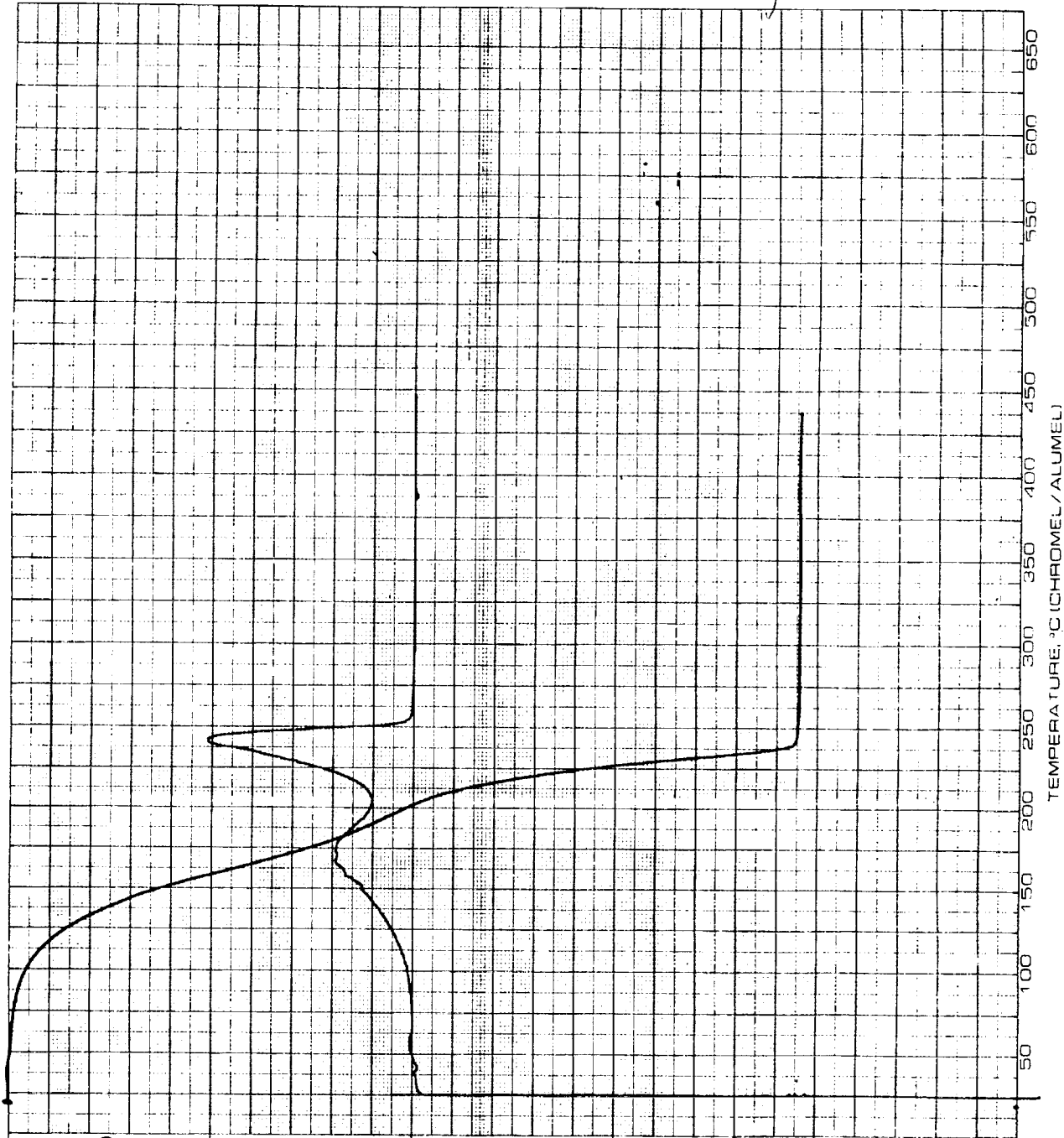
T-AXIS

PROG. RATE, °C/min 10  
 RANGE, °C/cm 25  
 HEAT COOL ISO  
 SHIFT, cm +10  
 TIME, min/cm 5

DSC 200  $\mu$ W/mV  
 DTA 50 mK/mV  
 RANGE, mV/cm  
 WEIGHT, mg  
 REFERENCE

TGA 50  $\mu$ g/mV DTG 50  $\mu$ g/(min mV)  
 SUPPRESSION, mg  
 RANGE, mV/cm  
 WEIGHT, mg  
 TIME CONST., sec  
 dY

TMA 1  $\mu$ m/min DIM 0.1  $\mu$ m/min  
 MODE  
 RANGE, mV/cm  
 SAMPLE SIZE  
 LOAD, g  
 dY



TEMPERATURE, °C (CHROMEL/ALUMEL)

Figure 3.9 Thermogram of Ink No. 9.



OMNI THERM CORPORATION

10°C/minute. Combined in Ink No. 3 and heated at the same rate they gave the thermogram of Fig. 3.10, which shows weight loss up to 360°C. Some organic reaction product was formed and this material required much higher temperature for burn-out than either of the ink ingredients. In general, all of the inks in Table 3.3 which had temperatures for complete carbon removal greater than 250°C had thermograms which showed a "tail" after the decomposition of the Ag neodecanoate at ~230°C similar to that for Ink No. 3 shown in Fig. 3.10.

A goal of this project is to develop a screen printable ink, and screen printing has been the primary method used for depositing films. Screen printing consists of forcing a high viscosity ink through a masked stainless steel screen and onto a substrate. The conductor test pattern used is shown in Fig. 3.11; it contains a serpentine segment for sheet resistance measurements, a segment for determining line definition, and 3 different sizes of square pads for adhesion testing. The substrates used in the initial stages of this study were 3M's AlSiMag 838 alumina, glass microscope slides, and silicon wafers. The goal is to deposit the films on silicon solar cells, but silicon substrates were used only very recently because the substrate holder on the screen printer had to be modified to accommodate them due to their small thickness. The screen printer used was an AREMCO Model 3100. Before the screen printer substrate holder was changed to accommodate silicon, or in situations where the ink was too thick to screen print, a simple method of doctor blading was substituted. This method involved putting a thin strip of ink on the substrate with a razor blade. The thickness was controlled by making a shallow channel with two strips of scotch

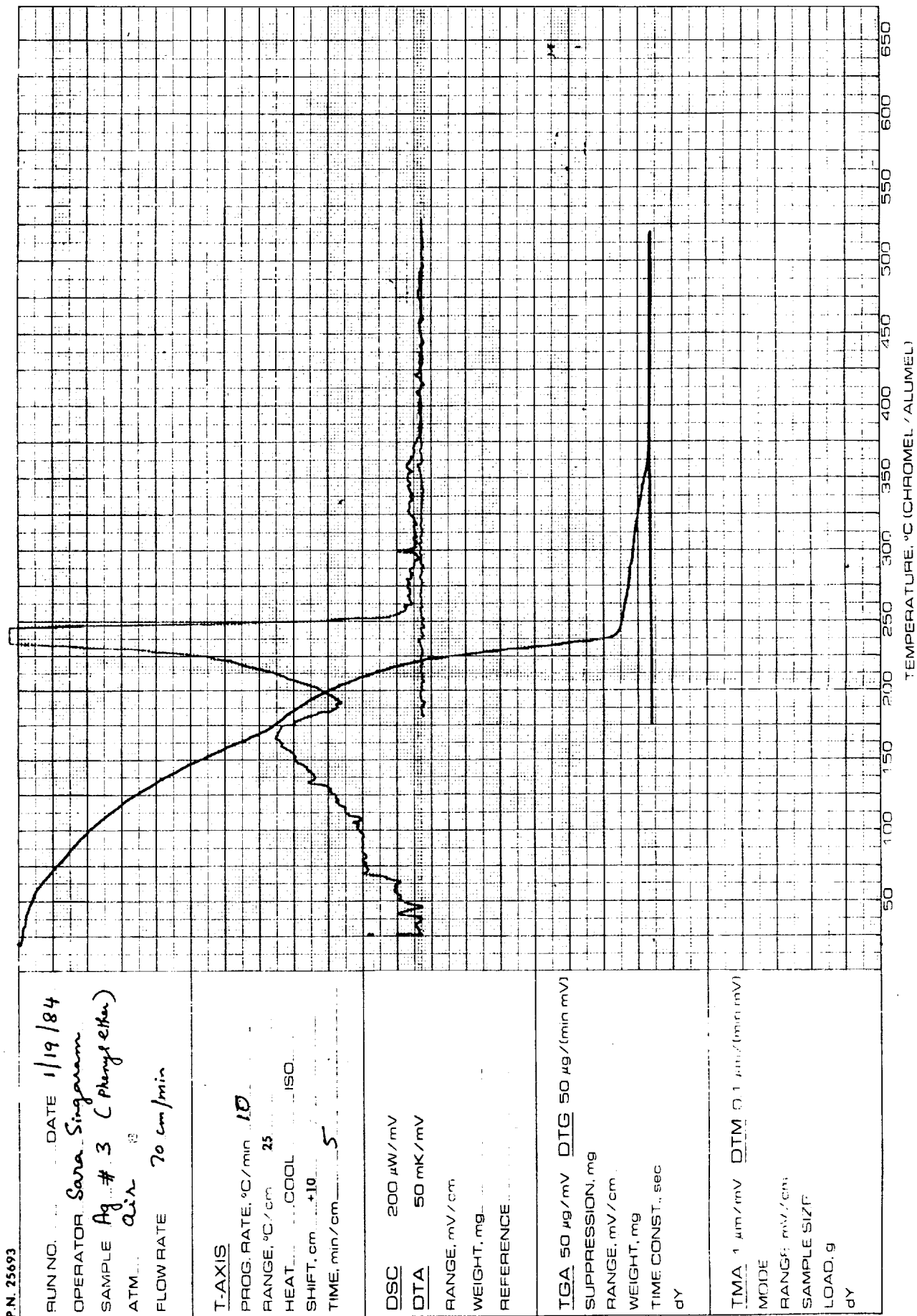


Figure 3.10 Thermogram of Ink No. 3.

Table 3.3 Formulation of Silver Inks.

Ink #	Method of Preparation	Additive	Approx. Comp. Ag Compd: Additive	w/o Ag by TGA	Temp. for Complete C Removal (°C)
1	A	$\alpha$ -terpineol BCA*	90:5:5	22	375
2	A	BCA	88:12	19	275
3	A	Phenyl ether	88:12	27	360
4	B	BCA	88:12	19	275
5	B	Dodecane	88:12	21	275
7	B	BCA	79:21	19	275
8	B	Dodecane	50:50	21	275
9	C	Neodecanoic Acid	not recorded	22	240
11	C	BBPE* BCA	85:5:10	16	212
12	C	Mineral jelly BCA	70:10:20	26	287
13	C	BPDA* BCA	86.5:3.5:10	30	240
20	A	xylene	-	28	250
21	A	Triglyme	90:10	30	244
22	A	Dodecane	95:5	30	235

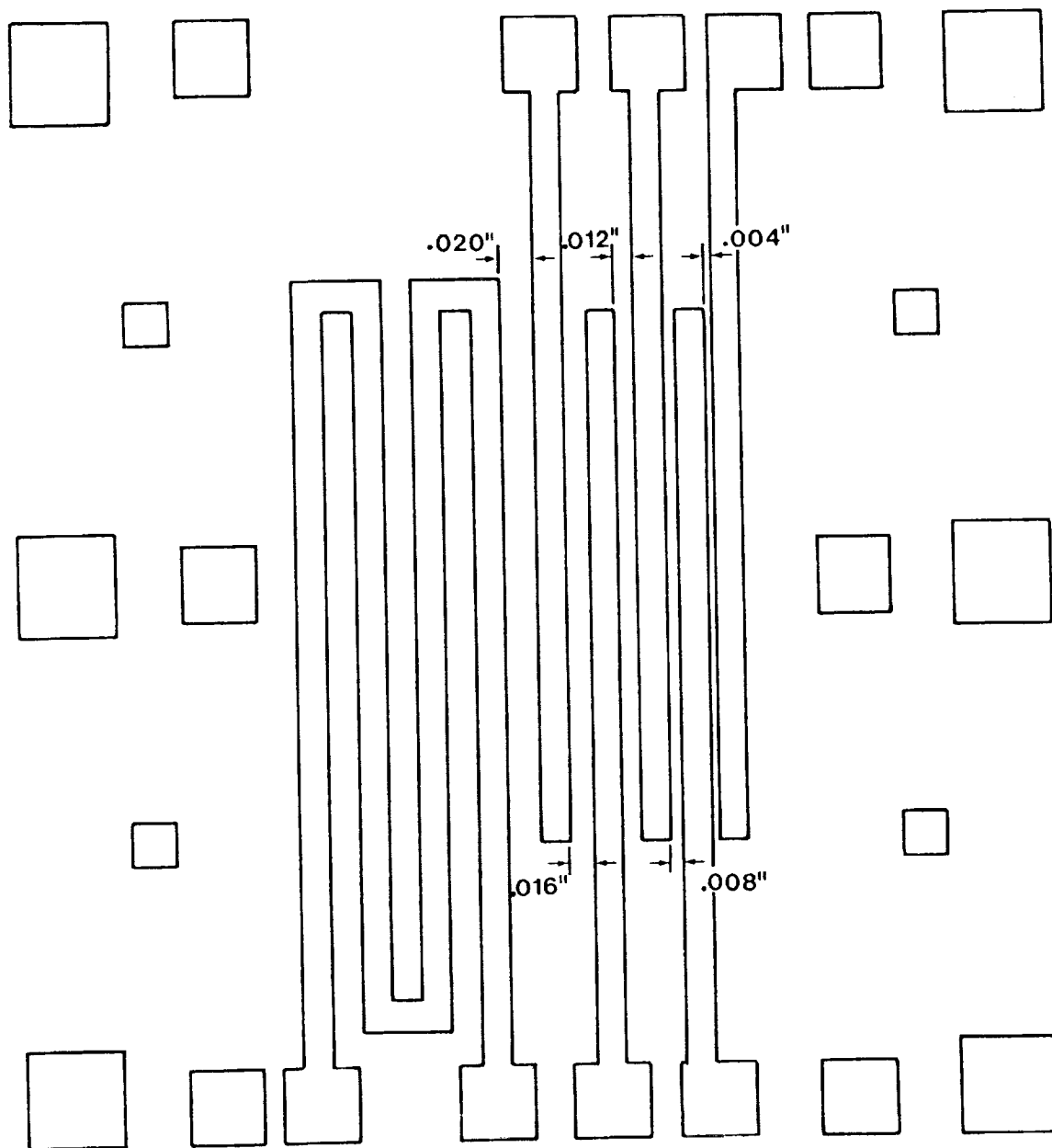


Figure 3.11 Conductor Test Pattern.

tape, and careful use of the razor blade gave film thicknesses approximately equal to that of the tape.

### 3.4 Firing

The most important consideration in the firing of the silver metallo-organic thick films for photovolatics is the maximum firing temperature, because the p-n junction is less than 0.5  $\mu\text{m}$  below the surface to be metallized. If the semiconductor is exposed to too high of a temperature, diffusion of the dopant atoms can occur and the p-n junction can be destroyed. Therefore, a maximum firing temperature of 350<sup>o</sup>C was chosen for the processing of the silver MOD films. This relatively low maximum firing temperature is one of the major reasons for the use of the silver MODS rather than conventional silver inks. Since there are no suspended particles in MOD inks, there is no need for high temperature sintering to obtain a good conducting film with good adhesion. With the MOD inks the maximum firing temperature needs to be only higher than the temperature at which complete decomposition of the ink occurs such that a continuous silver film results with good adhesion, resistivity and line definition. Of course, many parameters, besides the maximum firing temperature but connected with firing and other processing steps, have some influence over these film characteristics.

Another important firing consideration which relates to film quality and adhesion is that all solvents and screening agents must be removed prior to the beginning of silver film formation. If not, the silver film will be disrupted as the organic screening agents and solvent decompose mainly as volatile hydrocarbons, CO and CO<sub>2</sub>. In order



for this to be accomplished, an adequate drying step must precede any firing step. During the first weeks of this study it was believed that the silver film formation began at  $\sim 220^{\circ}\text{C}$  and suitable firing sequences were chosen with this in mind. However, more detailed TGA analysis of the silver neodecanoate revealed that the compound may begin to decompose to silver at temperatures as low as  $70^{\circ}\text{C}$  even though the majority of the decomposition occurs between  $150\text{--}225^{\circ}\text{C}$  (see Fig. 3.5). Therefore, some significant adjustments were made in the firing sequences used so that most, if not all, of the solvents and/or screening agents would be removed prior to any silver film formation.

A third important consideration in firing involves the use of thermodynamic phase stability plots to give guidance toward selection of a proper firing sequence. These plots allow for a determination of which phases, of any given system, will be stable at a given oxygen partial pressure and temperature. The system most important to the silver MODS is the carbon-silver system, and stability plots for carbon and silver with their respective oxides is shown in Fig. 3.12. Once these stability plots are obtained, a firing sequence can be chosen such that the temperature and oxygen partial pressure being used will only allow for the formation of silver, CO and  $\text{CO}_2$ . The formation of carbon and the silver oxides must be avoided since they will lead to poor overall film quality. Another parameter available from these plots is the maximum temperature at which silver oxidizes in air ( $P_{\text{O}_2} = .21 \text{ atm}$ ). As can be seen in Fig. 3.12, this temperature is approximately  $148^{\circ}\text{C}$  for silver. Therefore, once the silver film has been formed it should not be exposed to temperatures much above room temperature and below  $148^{\circ}\text{C}$  for any sig-

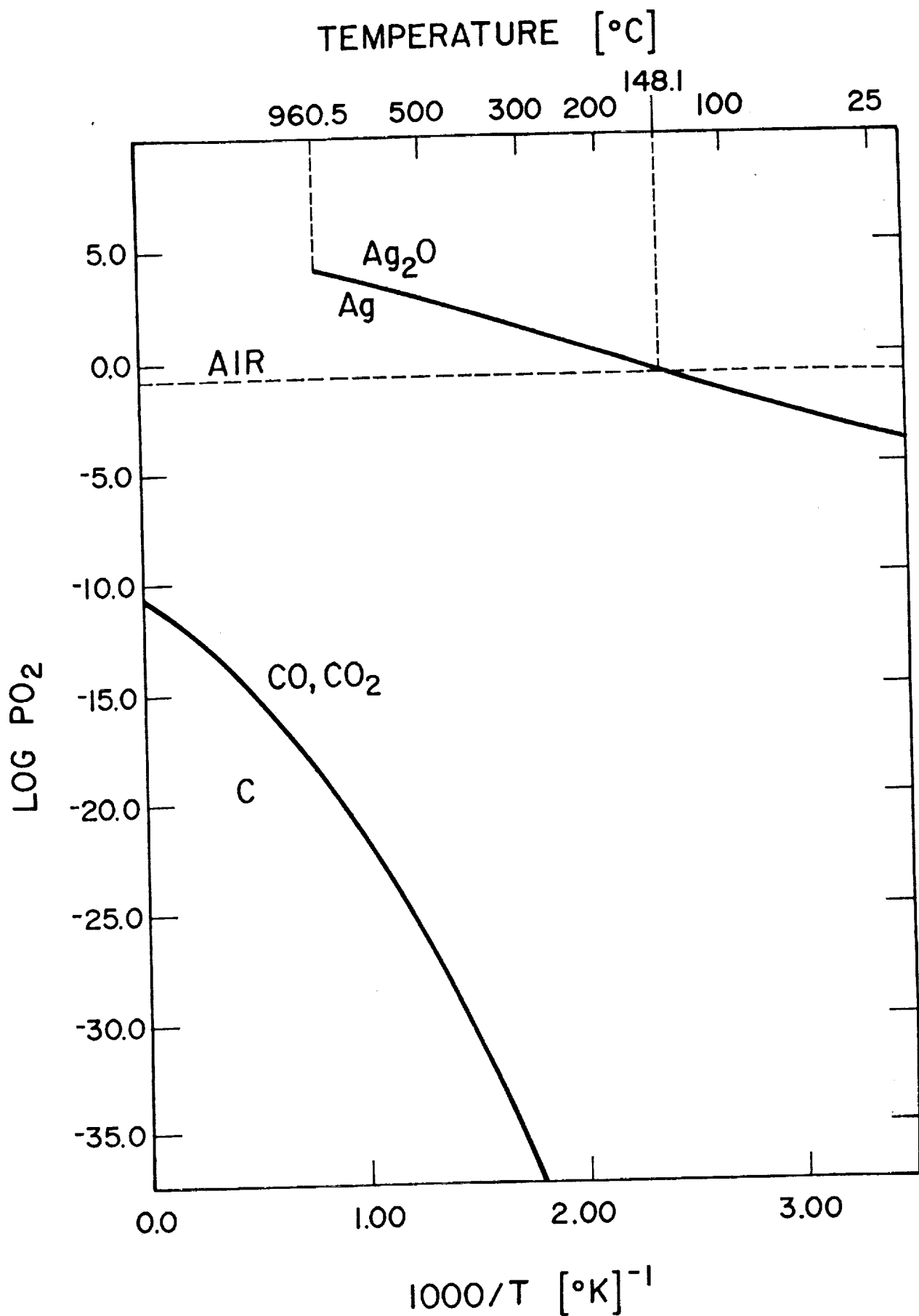


Figure 3.12 Phase Stability Diagram for the Ag - C - O System.

nificant length of time or the silver would be expected to oxidize to  $\text{Ag}_2\text{O}$ . However, it should be noted that these plots do not deal with the kinetics of silver oxidation, so the extent of oxidation at temperatures below  $148^\circ\text{C}$  as a function of time is unknown.

Four types of firing that have been used to date in the silver MOD study. They were:

1. muffle furnace at constant temperature and still air;
2. muffle furnace with time-temperature programming and controlled air flow;
3. belt furnace with variable time-temperature profiles and natural convection; and
4. combinations of No. 1 and No. 3.

Since the initial research was focused on developing an ink chemistry which will yield films of suitable quality in terms of appearance and adhesion, extensive firing tests with any one ink have not been conducted. However, a variety of firing sequences were used for each ink printed. In some cases a variety of furnaces and firing times and temperatures were used while in others firing at one temperature and time only was performed. The firing steps served only to aid in making a quick evaluation of the ink's potential and no attempt was made with any of the inks to optimize the firing sequence. However, a careful examination of the results will reveal some general patterns in the firing sequences used. Some type of drying step was usually used since, as was mentioned previously, it was recognized that the solvents and screening

agents had to be driven off before the silver film began to form. Prior to January 31st the drying temperature was usually in the 150°C vicinity. However, once the low (approx. 75°C) silver neodecanoate beginning decomposition temperature was discovered, a drying step was introduced in the 60-70°C temperature range for much longer times than had been used prior to January 31st. The drying step was usually omitted for a few samples from each ink to observe the effects of immediate firing after printing. However, it appears that the drying step for solvent and screening agent removal is essential if adequate film adhesion is to be obtained. This will be discussed further in the results and discussion section.

Following the drying step a very wide range of firing sequences were used to date, but the maximum firing temperature was always limited to 350°C or less. The length of various firing steps ranged from 10-60 minutes, with most in the 15-30 minute range. Firing rates also varied depending on the furnace used. For batch firing (system 1) the furnaces were capable of heating rates up to 30°C/minute, and batch fired samples were both fired at single temperatures and over a range of temperatures. For belt furnace firing, a wide variety of time-temperature profiles were possible, but were very time consuming to adjust. The small programmable muffle furnace provided the widest controlled range of firing sequences. The furnace used a 570 series Barber Colman programmer - controller, and was capable of accepting heating rates to 120°C/minute. The furnace could also be used with a wide variety of atmospheres.

#### 4. RESULTS AND DISCUSSION

Each of the inks listed in Table 3.3 was screen printed onto alumina substrates and fired to produce a silver film. The films were evaluated in terms of film quality (appearance), line definition, sheet resistance and adhesion. A summary of the results along with the type of furnace and the firing sequence used for each ink is contained in Table 4.1.

Film quality was judged by visual inspection, and the characteristics looked for were color and uniformity. The color should be silver if proper decomposition of the ink occurs during firing, but a wide variety of film colors have been observed ranging from a whitish silver to a dark black/brown. The majority of the films were a dark shade of grey. This non-silver color is probably due to one of two things: either there is some impurity still present in the inks despite the extensive purification, or the firing sequences used caused the silver neodecanoate plus additive(s) to decompose into unexpected by-products which appear as a dark residue on the films surface. In all cases, the dark surface film could be mostly removed by light burnishing with a pencil eraser revealing a silver film beneath. Also, the surface film could be removed by firing at 500<sup>o</sup>C for 10 minutes, but the adhesion was observed to degrade. There did not appear to be any correlation between surface appearance and any other of the film properties evaluated, and the nature of the surface film appears to be more dependent on ink chemistry than on the firing sequence used.

Table 4.1 Properties of Fired Silver Films on Alumina Substrates Unless Otherwise Noted.

Ink #	Firing Sequence		Type of Furnace*	Surface Appearance	Line Defin.	Sheet Resist. ( $\Omega/\square$ )	Adhesion
	Temp. °C	Time (min)					
1	25 120 200-350 350	10 10 10°/min. 8	1	dark green	fair to good	$\infty$	-
2	100 220 220-350 350	20 5 10°/min 17	1	light brownish yellow	fair to good	0.89- 2.68	-
2	25-75 75-285 285	5°/min 8.4°/min 5 min	3	grey silver	fair to good	0.259- 0.817	-
3	25-75 75-310 335	5°/min 8.4°/min 5	3	dark brownish grey	fair to good	2.19- 6.00	-
4	25-75 75-310 310	5°/min 8.4°/min 5	3	greyish silver	fair to good	>9.7	fair
5	25-75 75-310 310	5°/min 8.4°/min 5	3	greyish silver with brown tint	fair to good	3.07- 5.37	fair to good
7	25-75 75-310 310	12.5°/min 21°/min 2	3	greyish silver	fair to good	0.394- 0.411	fair to good
8	25 200-350 350	15 30°/min 20	1	yellowish silver with brown residue around fired pattern	poor	0.161- 0.234	poor

\*See Section 3.4

Table 4.1 Continued

Ink #	Firing Sequence		Type of Furnace*	Surface Appearance	Line Defin.	Sheet Resist. ( $\Omega/\square$ )	Adhesion
	Temp. °C	Time (min)					
9	200-350 350	10 <sup>o</sup> /min 20	1	silvery surface with yellow tint	poor	0.113-0.112	poor
11	200-350 350	10 <sup>o</sup> /min 30	1	brownish black with oily texture	excellent	∞	poor to fair
12	100 200-350 350	15 10 <sup>o</sup> /min 45	1	brownish grey	poor <sup>a)</sup>	not measured	poor <sup>a)</sup>
20	70 200 200-250 250 350	15 10 10 <sup>o</sup> /min 10 30	1	brownish grey	good 0.008"-0.012"	0.460-5.36	good to excellent
21	60 200 225 350	30 20 20 30	1	dull yellowish silver	fair 0.020"	0.189	good
21	60 200 225 350 350-500 500	30 20 20 30 30 <sup>o</sup> /min 12	1	whitish silver	fair	0.062	poor to fair
21 <sup>b)</sup>	60 200 350	40 20 30	1	brownish grey yellow	fair	0.280-0.626	good
22	65 200 200-300 300	30 20 10 <sup>o</sup> /min 25	1	grey with gold tint	fair 0.016"	0.078-0.121	good to excellent
22	65 25-70 70 70-200 200 200-300	20 5 <sup>o</sup> /min 15 5 <sup>o</sup> /min 20 5 <sup>o</sup> /min	2	yellowish grey silver	fair 0.012-0.016"	0.083-0.103	fair to good

a) good to excellent on glass

b) printed and fired on Si

Line definition was evaluated both visually and by resistance measurements using the conductor pattern shown in Fig. 3.11. The separation between adjacent lines decreases from .020" to .004" in increments of .004", so by making resistance measurements between the end pads of adjacent lines a quick line definition test can be conducted. If a resistance is measured between adjacent lines it means they are in contact with each other at least one point, and the line definition at that separation distance is not good. Such measurements allow line definition to be reported quantitatively in terms of a minimum distance for which separation still exists. The smaller this distance, the better the line definition. As can be noted in Table 4.1, line definitions were measured qualitatively (visually) for the most part since the conductor pattern shown in Fig. 3.11 was not initially available. However, quantitative measurements were made for films produced from Inks 20, 21 and 22.

Sheet resistance of the films was measured using the serpentine section of the conductor pattern shown in Fig. 3.11. This part of the pattern has 103 squares, and the sheet resistance was calculated by dividing the measured resistance by the number of squares to give a sheet resistance in ohms per square. To determine the resistivity for comparison with pure silver, the sheet resistance must be multiplied by the fired film thickness, but the fired films are too thin to measure their thicknesses directly on the light-section microscope, and are too soft to measure with our moving stylus instrument. The fired film thickness will be calculated in future studies by using a theoretical film volume change during firing obtained from measuring the dried film



thickness with the light section microscope. The wide variation observed in sheet resistance is indicative of large differences in film microstructure, which is determined by the combination of ink chemistry and firing sequence. However, there is no obvious correlation between sheet resistance and the processing variables.

The majority of the effort during this first quarter of the project was devoted to studies of the adhesion of the MOD silver films to the substrate. The ASTM definition of adhesion is the "state in which two surfaces are held together by interfacial forces which may consist of valence forces, interlocking forces or both". A considerable amount of work as gone into understanding the mechanisms of thick film adhesion, but it seems more is known about why things don't stick than why they do. Low firing silver neodecanoate inks have produced adhering films on all types of substrates under the proper processing conditions, although long term adhesion has not been determined. No attempt has been made, to this point, to study the mechanism responsible for this adhesion but more extensive studies will be done once a suitable group of screen printable inks have been developed.

The most common adhesion tests for thick film conductors involve soldering wires to pads on the substrate and measuring the force required to separate the film from the substrate. Ink development to date has concentrated on pure silver inks, and pure silver is very soluble in tin-lead solders. Therefore, the more quantitative adhesion tests could not be used. The test used was the Scotch tape test, which involves placing a piece of Scotch tape across the film, smoothing out any air bubbles, and then pulling the tape up as evenly and uniformly

as possible. The degree to which the film is removed by the tape allows for a quick, qualitative measurement of adhesion. The four ratings for this adhesion test are excellent (95-100% adhesion), good (75-95% adhesion), fair (50-75% adhesion) and poor (<50% adhesion). Excellent adhesion in the Scotch tape test is generally considered the minimum acceptable adhesion for the silver MODS on silicon or other substrates. The next phase of ink development will involve the addition of approximately 4 w/o platinum to prevent solder leaching so that more quantitative adhesion tests can be performed.

Initially, the temperature at which silver neodecanoate begins to decompose was believed to be in the 220°C range and drying temperatures of 100°C or higher were used during batch firing and little importance was placed on heating rate during belt firing (ink Nos. 1-9 in Table 4.1). Once the adhesion problem was discovered, an attempt was made to add boron or silicon metallo-organic compounds as flux bonders to aid in adhesion. It was hoped that the boron might react with the  $\text{SiO}_2$  monolayer on silicon or  $\text{Al}_2\text{O}_3$  in the alumina substrates to form a glass which would act as an adhesive similar to flux bonders in conventional thick film inks. However, these experiments resulting in non-adhering, non-conducting, black/brown films (e.g., Ink No. 11 in Table 4.1).

The search for a flux bonder was abandoned, at least temporarily, when the TGA of a new batch of purified silver neodecanoate was run and the low beginning decomposition temperature was discovered. The approach was then taken to try longer drying times at lower temperatures before firing to see if adhesion could be influenced in a positive manner. Three inks were tried with this adjustment in processing (ink

Nos. 20-22 in Table 4.1), and good to excellent adhesion was obtained in many cases where 15-30 minutes of oven drying was done in the 60-70°C range. Unfortunately, the overall film quality in terms of appearance was not as good as desired so the problem has not been fully solved. There is no question but that adhesion is related to solvent removal. It has been shown that it is very important to remove all solvents and screening agents prior to the beginning of silver film formation, and the TGA in Fig. 3.5 shows that silver neodecanoate solid may actually begin to decompose at temperatures as low as 75°C. If any solvents come off after the silver film begins to form it will be disrupted and most likely have a significant affect on adhesion.

## 5. FUTURE PLANS

The immediate future work will concentrate on combining the decent film appearance of earlier inks with the good to excellent adhesion of the most recent inks. Some differences between Inks 7, 8 and 9 and Inks 20, 21 and 22 are that each set was made from different batches of solid silver neodecanoate which were prepared in slightly different ways, especially in terms of purification procedures. The silver neodecanoate for Inks 7, 8 and 9 was either mixed directly with a screening agent as for Ink 9 or was dissolved in the solvent toluene first, while Inks 20, 21 and 22 used silver neodecanoate dissolved in xylene. This difference between toluene and xylene solvents may prove to be very important. During evaporating of the solvent, which is done to get an ink of the proper rheology, the solution is heated to 50-60°C at 12-14 mm pressure for xylene solutions of silver neodecanoate. These temperatures are very close to the temperature at which silver neodecanoate may begin to decompose. Toluene, on the other hand can be evaporated off at a much lower temperature, and if benzene is used as a solvent it can be evaporated off at still lower temperatures. Therefore, the next set of inks will be made with either purified solid silver neodecanoate dissolved in toluene or benzene instead of xylene, or mixed directly with a screening agent without the use of a solvent. These inks will then be dried below 70°C after printing and will, hopefully, lead to fired films with good adhesion as well as more silvery appearance and good line definition. Recall that Inks 7, 8 and 9 used higher drying temperatures for generally shorter times, and the solvents and screening agents may not have been driven off before the silver film began to form.

The other area of work in the near future will be to further evaluate the affect of the flowing air atmosphere and the importance of the 150-225°C firing range. Various heating rates will be investigated in the programmable batch kiln furnace and also in the new IR furnace which is expected to be in operation in the near future. Once a more suitable fired film is obtained in terms of overall film quality and adhesion, several longer range studies can begin. These include the addition of platinum to the ink so that quantative adhesion data can be obtained, and a study of the mechanism of adhesion.

## 6. SCHEDULE

The updated program plan is attached. All milestones have been reached as scheduled, except for the distribution of this report which was delayed until a distribution list was received from JPL.

[illegible]

12/1/83	2/1/84	4/1/84	6/1/84	8/1/84	10/1/84	12/1/84	2/1/85	4/1/85
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